



3 1176 00167 5934

NASA CR 165,292

NASA CR - 165292



NASA-CR-165292
19810011716

PASSIVATION OF CARBON STEEL THROUGH MERCURY IMPLANTATION

PREPARED FOR
LEWIS RESEARCH CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GRANT NAG-3-25

LIBRARY COPY

APR 6 1981

LEWIS RESEARCH CENTER
LIBRARY, NASA
HAMPSHIRE, VIRGINIA

Final Report

February 1981

Paul J. Wilbur and Raymond S. Robinson
Department of Mechanical Engineering
Colorado State University
Fort Collins, Colorado

1. Report No. NASA CR 165292		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Passivation of Carbon Steel Through Mercury Implantation				5. Report Date Feb. 1981	
				6. Performing Organization Code	
7. Author(s) Paul J. Wilbur and Raymond S. Robinson				8. Performing Organization Report No.	
9. Performing Organization Name and Address Department of Mechanical Engineering Colorado State University Fort Collins, Colorado 80523				10. Work Unit No.	
				11. Contract or Grant No. NAG-3-25	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				13. Type of Report and Period Covered Feb. 1, 1980 - Feb. 1, 1981	
				14. Sponsoring Agency Code	
15. Supplementary Notes Grant Monitor - William Kerslake, NASA Lewis Research Center, Cleveland, Ohio 44135.					
16. Abstract An experiment, in which carbon steel samples were implanted with mercury ions from a broad beam ion source and their corrosion characteristics in air were evaluated, is described. Mercury doses of a few mA min/cm ² at energies of a few hundred electron volts are shown to effect significant improvements in the corrosion resistance of the treated surfaces. In a warm moist environment the onset of rusting was extended from 15 min. for an untreated sample to ~ 30 hrs. for one implanted at a dose of 33 mA min/cm ² with 1000 eV mercury ions.					
17. Key Words (Suggested by Author(s)) Broad Beam Ion Source Corrosion				18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 34	
				22. Price*	

* For sale by the National Technical Information Service, Springfield, Virginia 22161

TABLE OF CONTENTS

<u>Topic</u>	<u>Page</u>
Abstract	i
Introduction	1
Background	1
Experimental Apparatus and Procedure	3
Test Samples.	4
Mercury Implantation.	5
Sample Oxidation.	8
Theoretical Basis for the Interpretation of Reflectance Measurements	10
Results.	14
Additional Results.	20
Conclusion	20
References	22
Appendix A - The Qualities of and Equipment for Ion Implantation.	23
Appendix B - Reflectance Measurements, Mercury Implanted Carbon Steel.	27

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page</u>
1.	Broad Beam Ion Source Current Density Profile	6
2.	Test Sample Reflectance Characteristics.	11
3.	Time History of Carbon Steel Corrosion in Warm, Moist Environment	15
4.	Effects of Oxidation Temperature	18
5.	Effects of Implanted Mercury Dose and Energy	18

PASSIVATION OF CARBON STEEL THROUGH MERCURY IMPLANTATION

During the course of the development of a mercury, electron-bombardment thruster in England, a group of researchers placed a carbon steel plate in the beam of the thruster as part of a facility checkout test. After a few days in the facility the plate was removed and placed in the ambient, outdoor environment. A few years later someone noticed that the plate was rusted over all of its surface except that region where the mercury ion beam had impinged upon it.¹ The tests described in this report were designed to investigate this phenomenon of the inhibition of carbon steel corrosion by implanted mercury ions under more closely controlled experimental conditions. The purpose of this work has been to identify the mercury ion doses and energies required to induce this beneficial rust resisting treatment of carbon steel surfaces. The work must be considered preliminary because much of it has been directed at designing procedures and defining the range over which the parameters show significant effects rather than executing a statistical study involving large numbers of test samples.

BACKGROUND

While the phenomenon observed by the English thruster researchers awakened interest in mercury implantation as a means of inhibiting carbon steel corrosion, the process of implantation has been under investigation for some time. The basic process, which evolved initially in the semiconductor industry, has been recognized as useful for a variety of surface treatments designed to improve hardness, wear resistance, and fatigue

lifetime in addition to the corrosion resistance of various materials.^{2,3,4} This interest in applications other than those related to semiconductors has however evolved within the past several years.

The basic process of ion implantation involves directing high speed ions at a surface in a vacuum environment. Some of the ions are captured in the material being bombarded in such a way that they can act to change the physical properties on the surface of the material. Ion implantation differs from such conventional processes as electroplating or vapor deposition in that it effects a chemical or physical composition change near the surface of the base material. Some of the advantages of ion implantation over conventional plating, surface treating or alloying procedures, which have been identified, are listed in Appendix A. Chief among these advantages is the capability for implanting almost any ionic species into any solid material without introducing undesirable dimensional changes or thermally induced transformations. Since the implanted ions do not represent a coating, adhesion and peeling problems which can be induced by inadequately cleaned surfaces and by thermal and mechanical stresses in deposited films are also eliminated.

The potential for the application of this technology in the metallurgical industries is truly phenomenal if the cost of the process can be held at an acceptably low level. The basic research into these phenomena seems however to have been carried out using equipment designed for ion implantation in semiconductors and this equipment is relatively expensive to both purchase and operate. It has capabilities that are however probably not required in metallurgical applications. For example the high purity beams produced for semiconductor treatments are almost certainly unnecessary. The high ion energies needed to produce acceptable current

densities in these high purity implanters are also probably not required in the metallurgical applications. Finally, the typical single aperture ion implantation source has a very small areal coverage. Considerably higher current densities, the capability for handling larger metallurgical targets with lower capital investments in equipment and lower operating expenses can be realized if multiaperture, broad beam ion sources are used. These broad beam ion sources, developed initially for space propulsion use, are just beginning to find application in the electronics industry. The differences between the single aperture implanter and the broad beam ion source are illustrated by the comparison of performance capabilities given in Appendix A.

While it is difficult to anticipate the potential applications of a simple scheme for inhibiting rust formation it would seem likely that it might find initial application in protecting small tools such as those used in the electronics, medical and dental areas. This procedure might make it possible to make such tools out of conventional steels rather than the more expensive stainless steels. Razor blades and certain decorative trims represent other areas where ready markets for such a process might be found. Eventually one might envision large vacuum facilities and ion sources capable of handling individual items as large as vehicle components. Assuming the process is successful one could also foresee this type of corrosion protection applied to metals other than steels which tend to tarnish.

EXPERIMENTAL APPARATUS AND PROCEDURE

The basic objective of the experimental work described in this report has been to demonstrate the beneficial effects of implanted

mercury in inhibiting the corrosion of carbon steel. Two parameters associated with the implanted mercury were identified as important, namely the dose of the delivered mercury ions and their energy of impact. To first order the dose determines the degree of coverage while the energy determines the depth of penetration of the mercury ions.

The procedure followed in the conduct of the experiment was to first clean some carbon steel samples chemically, then to expose them to a mercury ion beam characterized by an energy and a current density for the time required to produce the desired dose. After implantation the samples could be exposed to either a dry, oven environment or to a moist, warm air environment to effect oxidation. Finally the reflectances of samples implanted at different dose and energy levels and exposed to different oxidizing environments were compared. Reflectance was selected as the basis of comparison for this preliminary test because it can be measured easily and it is the property that is of primary importance in determining the aesthetic appeal of a surface.

Test Samples

All carbon steel test samples used in the study were cut from a single sheet of 22 gauge, cold rolled steel as supplied by a local steel yard. This steel, designated ASTM-A-366, QQ-698, contains 0.15% carbon, 0.25 to 0.60% manganese, 0.35% max phosphorus and 0.040% max sulfur. The rectangular samples cut from this material were 1.1 cm x 1.7 cm. After considering several possible cleaning alternatives the one yielding the most reproducible reflectance measurements after oxidation in a dry oven environment was selected. This procedure involved a one minute sequential immersion in the following chemicals:

1. Chloroethene (degreaser)
2. 18.5 weight percent hydrochloric acid
3. Distilled water
4. Methanol
5. Acetone

After immersion in each chemical the samples were dried with a tissue before immersion in the next one. After the chemical cleaning the samples were placed in a vacuum environment for storage. Although no oxidation of the samples was evident when the samples were stored in an ambient air environment they were always kept in vacuum storage as a precaution against inadvertent differential oxidation of samples because they were exposed to ambient air for the different periods of time.

Mercury Implantation

Implantation was effected in a 45 cm dia. vacuum facility. The broad beam ion source used to accomplish this was a 15 cm dia. multipole design with its grid masked down to a 10 cm dia. A typical current density profile from the source, this one for a 200 eV ion energy, is shown in Fig. 1. Test samples to be implanted were placed 6 cm downstream of the grids within the central 3 cm radius circle where the current density was very uniform. During implantation the background mercury pressure was typically 3×10^{-5} torr. Implantation of the test samples was accomplished by placing an array of twenty samples in the vacuum facility, downstream of the ion source. The system was pumped down to 1×10^{-6} torr before the working fluid was introduced into the system. Next, stable ion source operation was achieved with a shutter located 3 cm downstream of the ion source grids positioned to shield the samples. After the desired current

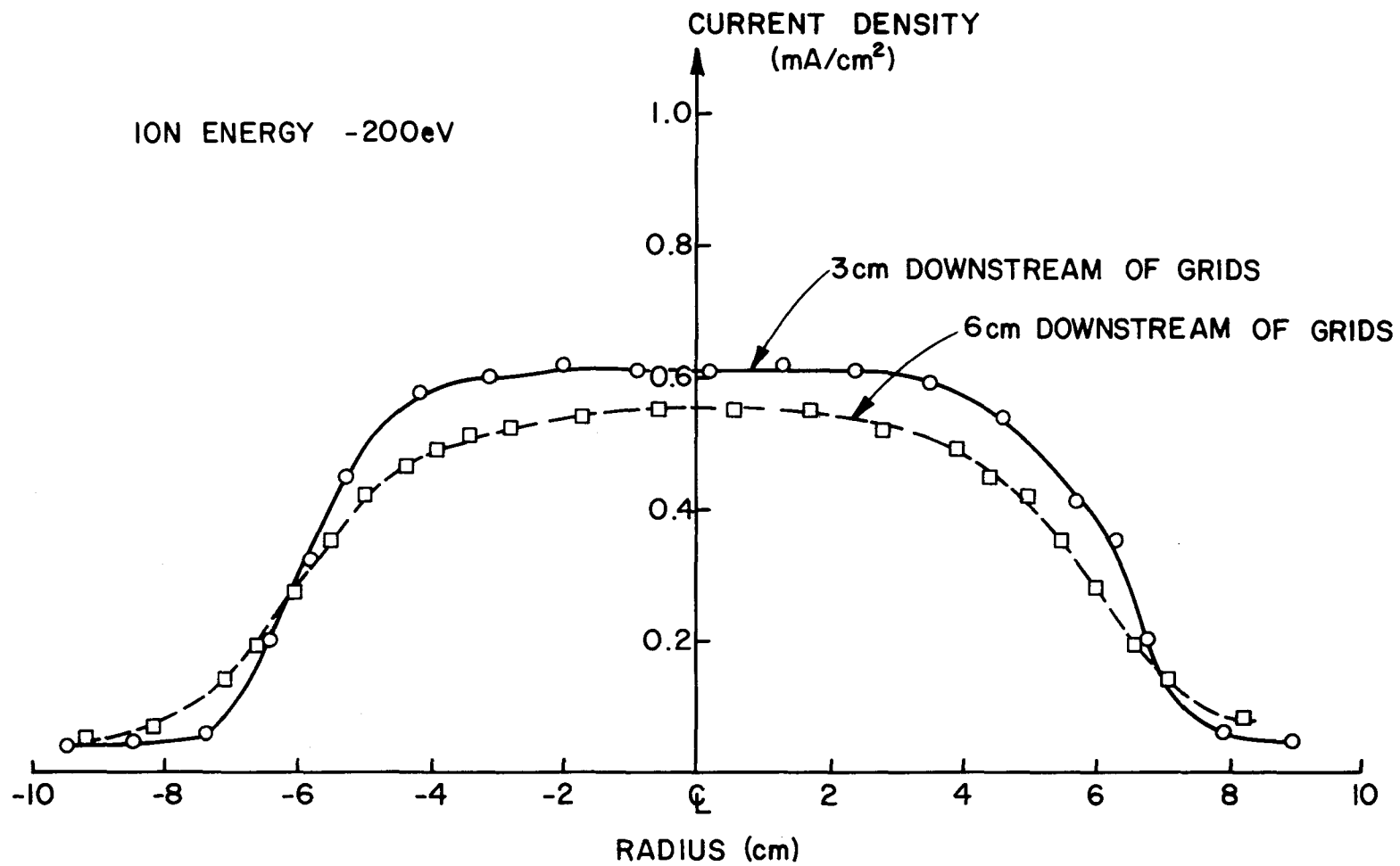


Fig. 1. Broad Beam Ion Source Current Density Profile

density and ion energy operating conditions had been established the shutter was opened and the twenty samples were implanted simultaneously for the time necessary to produce the desired dose. The shutter was also equipped with a Faraday current density sensor that could be used to verify the uniformity and constancy of current density from one implantation run to the next. During exposure the samples were cooled radiatively and measurements on a set of dummy samples suggested their temperature rose rapidly to a value of 120 to 140°C when they were exposed to the ion beam. Typically their temperature had risen through 90% of the total temperature rise within about 7 minutes after the shutter had been opened. The samples were allowed to cool under vacuum for several hours after they had been implanted.

On the basis of a few preliminary tests, ion energies of 200 eV and doses as low as 5 mA min/cm² were shown to effect some improvement in corrosion resistance of the carbon steel. As a result of this observation ion doses of 1.1, 2.8, 5.5, 11 and 33 mA min/cm^{2*} and energies of 200, 500 and 1000 eV were selected as reasonable values which would show significant changes in the corrosion resistance of the carbon steel samples. Tests executed after the preliminary ones were therefore conducted on samples that had been treated with all possible combinations of the doses and energies cited above.

* These doses correspond respectively to 4.1×10^{17} , 11×10^{17} , 21×10^{17} , 41×10^{17} and 120×10^{17} mercury ions/cm².

Sample Oxidation

Oxidation was effected by two separate procedures, one in which moisture was supplied to accelerate the process and a second in which the dry air was used. When the second procedure was followed, oxidation was accelerated by exposing the samples in an oven operating at temperatures in the 175 to 225°C range. The tests in which moisture was present were conducted first by simply placing a fixture containing an array with one each of the samples (each dose and energy combination) in the outside ambient weather. These samples were oriented so the treated surface was facing the sky and their condition was monitored weekly over the four month period from October 1980 through January 1981. It appeared that atmospheric, particulate fallout was dominating the initiation of rust spots and since the distribution of this fallout was not controlled it appeared to be introducing errors into the test results. To correct the problem statistically would have required that the test be conducted with many times the samples and this was not possible with the given time and resource constraints.

A test was next performed by exposing an array of samples (one for each dose and energy combination) to a moist, warm laboratory environment. This environment was created in a small polyethylene film tent wherein moisture from a pan of boiling water was circulated along with air over the samples. The implanted surfaces of the samples were oriented upward and moisture from the >100% relative humidity, 60°C air condensed on the samples as they were being oxidized. After several minutes of exposure these samples began to show signs of rusting and after several hours they were all rusted to various degrees. It was observed during this test that the rust seemed to start at the edges of the test samples where the

mercury had not been implanted. After initiation these rust spots seemed to grow inward across the treated surfaces. A review of the samples that had been exposed to the outdoor weather, made after this observation, revealed that rusting had probably started on the edges of these samples and then grown inward over the implanted surfaces also.

A final test was set up in which the array of samples was prepared as it had been in the previous tests but the edges of each sample were sealed with epoxy before the array was placed in the moist, warm environment of the tent. The condition of the samples was monitored by removing them from the tent and photographing them at regular time intervals. Although some rusting still seemed to start at the edges of the samples as a result of moisture getting under the epoxy, this procedure seemed to extend the time to the initiation of rust spots on implanted samples and to produce consistent trends in the corrosion results.

In the second series of oxidation tests an array consisting of one sample of each combination of dose and energy along with an unimplanted sample was oxidized in an oven. A small compressor was used to circulate air continuously through a moisture absorption column and the oven during both a preheat period in which the oven temperature was stabilized at a preselected value and during the actual oxidation period. The samples were placed in the oven, after the oven temperature was stabilized. The temperature was maintained within $\pm 1^\circ\text{C}$ of the setpoint temperature over the duration of the oxidation period. Each array of samples was exposed to each combination of oxidation durations of 1 hr., 2 hr., 4 hr. and 8 hr. and oven temperatures of 175°C , 185°C , 200°C , 205°C , 215°C and 225°C . After oxidation these samples were transferred directly to a vacuum environment where they were allowed to cool. A total of 384

samples was required to complete this test matrix of four oxidation durations, at six oven temperatures, for samples having sixteen dose and energy states.

After the samples had been cooled they were placed in a Beckman spectrophotometer operating in the reflectometer mode and the total reflectance (i.e., over all angles) was measured at a wavelength of 6000 \AA . The reflectance of some samples was actually measured over the wavelength range from 4000 \AA to 7000 \AA . This produced reflectance profiles like the ones shown in Figure 2. The reflectances shown in Fig. 2 have been corrected for neither the slight zero drift that occurs as a function of wavelength nor the drop in reflectance of the calibration sample at low wavelengths so they are designated "not normalized." As the results of Fig. 2 suggest, the profiles of reflectance were not strongly dependent on wavelength so it appeared that reflectance comparisons between samples could be made at just one wavelength. A wavelength of 6000 \AA was selected as the value at which these comparisons would be made because the intensity of the spectrophotometer light source was high at this point. This ensured good instrument response could be achieved without the need for electronic compensation for light source intensity attenuation.

THEORETICAL BASIS FOR THE INTERPRETATION OF REFLECTANCE MEASUREMENTS

The essential assumption made in the oven oxidation reflectance measurement tests is that there is a correlation between the surface reflectance of a sample and the extent of its oxidation. In order to quantify the degree of oxidation of a sample and thereby facilitate comparison between samples it was assumed that the reflectance of a surface could be expressed as the linear mean of the microscopic reflectances of

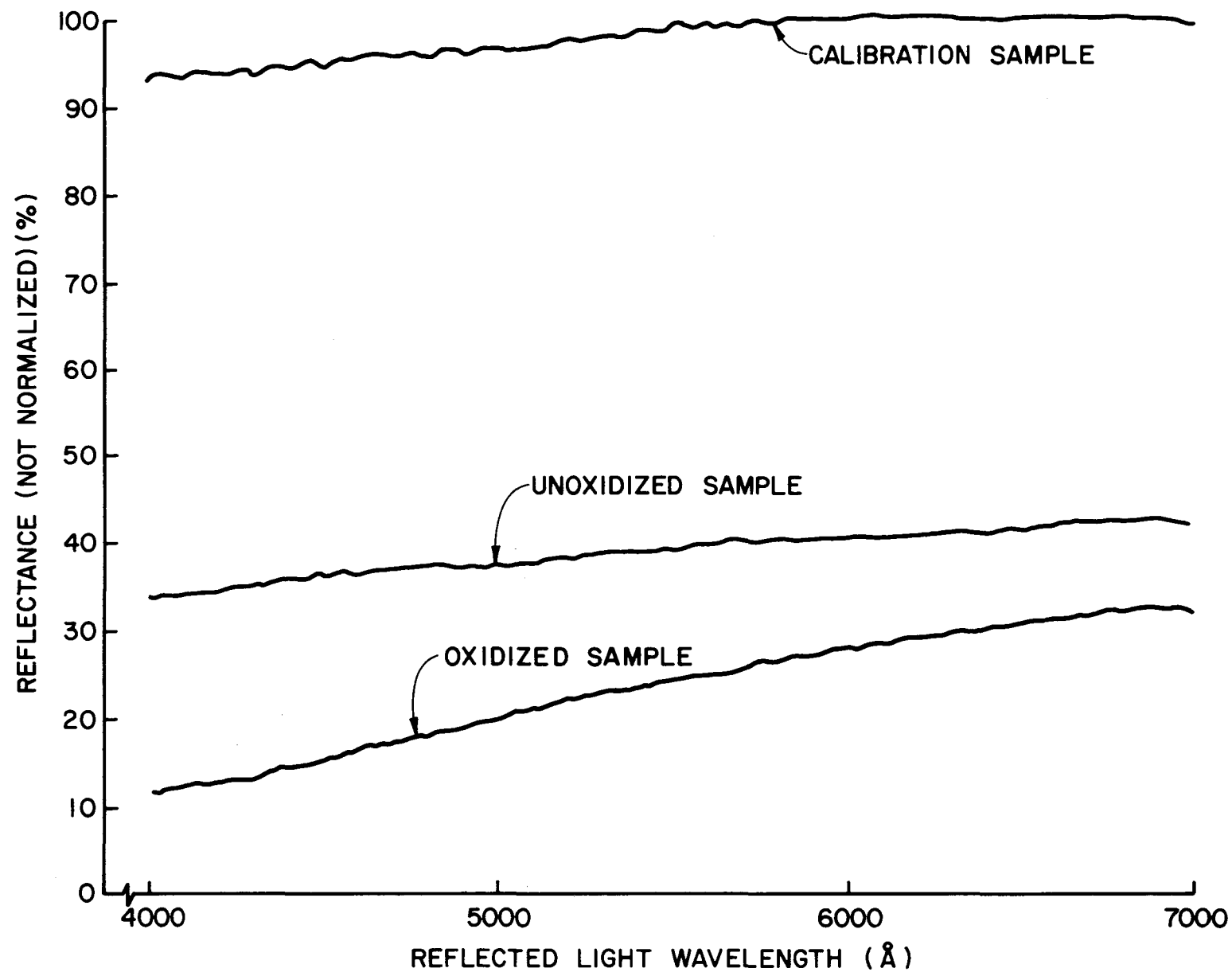


Fig. 2. Test Sample Reflectance Characteristics

a large number of sites making up the sample. The various sites considered to be available on a mercury implanted steel sample are identified by the following symbols:

FeO - Oxidized steel site

Fe - Unoxidized steel site

Hg - Unoxidized site protected by mercury

HgO - Oxidized site protected by mercury.

This basic assumption leads one to the following expression for the composite reflectance of a surface having surface site concentrations (c_i) with reflectances (r_i).

$$r = \frac{c_{FeO} r_{FeO} + c_{Fe} r_{Fe} + c_{Hg} r_{Hg} + c_{HgO} r_{HgO}}{c_{FeO} + c_{Fe} + c_{Hg} + c_{HgO}} \quad (1)$$

Reflectance measurements made on clean steel (Fe), mercury implanted steel (Hg) and heavily implanted steel that had been oxidized (HgO) suggested that the reflectances of each of these sites was essentially the same

$$r_{Hg} \approx r_{Fe} \approx r_{HgO} \approx 0.55$$

Using this result in Eq. (1) one obtains

$$r = r_{FeO} + f (r_{Hg} - r_{FeO}) \quad (2)$$

or

$$f = \frac{r - r_{FeO}}{r_{Hg} - r_{FeO}}$$

where " r_{Hg} " is the common reflectance of all sites that are not oxidized steel, " r_{FeO} " is the reflectance of a highly oxidized steel surface and " f " is the fraction of the surface that is unoxidized steel.

The basic rate equation for oxidation of the surface described as the rate of change of the fraction of the surface that is unoxidized steel and assuming ample available oxygen is⁵

$$\frac{df}{dt} = -k_f f^\alpha \quad (3)$$

In this equation k_f is the rate factor and it is assumed to be described by an Arrhenius expression⁵

$$k_f = A e^{-\epsilon_a/kT} \quad (4)$$

The quantity "A" is the frequency factor, k is the Boltzmann constant (8.6×10^{-5} eV/°K) and " ϵ_a " is the activation energy associated with the reaction (eV). The quantity " α " in Eq. 3 is the order of the reaction. For first order reaction ($\alpha = 1$) Eq. 3 integrates to

$$f = e^{-k_f t} \quad (5)$$

while non-first order reactions ($\alpha \neq 1$) give

$$f = [1 - k_f t]^{1/(1-\alpha)} \quad (6)$$

Equations 5 and 6 then describe the time variation of the fraction of a surface that is unoxidized in terms of the rate factor (k_f) and the order of the reaction (α). Inherent in these equations is the assumption that unoxidized surfaces exhibit the same reflectance regardless of the mercury dose and energy to which they have been exposed. Reflectance measurements made on a variety of unoxidized samples support this assumption. In order to determine the quantities k_f and α samples were oxidized for various lengths of time in an oven operating at a fixed temperature. Reflectances were measured for each of the oxidized surfaces and these

data were used in Eq. 2 to determine the fraction of the surface that remained unoxidized after exposure to the oxidizing environment. The data were then fitted to either Eq. 5 or Eq. 6 to determine the numerical values for k_f and α pertaining to the specified oxidation temperature and test sample state. By using the same analysis on other test samples prepared at the same mercury dose and energy but oxidized at different oven temperatures one can, by using Eq. 4, determine the activation energy (ϵ_a) and frequency factor (A) appropriate to each implanted mercury dose and implantation energy state of the samples.

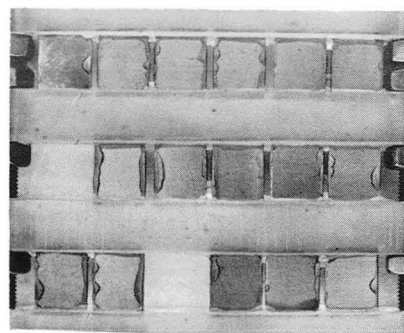
RESULTS

Samples exposed to a warm, moist environment showed a rapid tendency to oxidize if they were not treated using mercury implantation. Evidence of the beneficial effect of implanted mercury in this oxidizing environment is given in Fig. 3. This figure shows a photographic time history of the oxidation of an array of the samples subjected to the mercury ion dose and energy combinations mentioned previously. The key in the upper left hand corner of the figure identifies the mercury ion dose (mA min/cm^2) and energy (eV) treatments pertaining to the samples in the photographs. A type 304 stainless steel sample and a carbon steel sample that received no mercury treatment are also identified in the key and shown in each photograph to facilitate comparison.

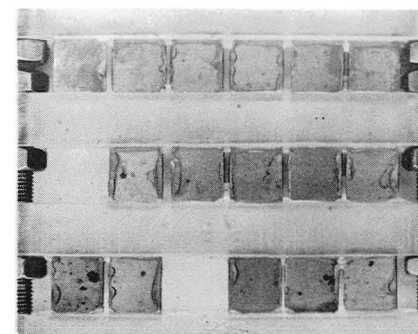
Initially (zero hr.) the samples are observed to be quite uniform in appearance. The epoxy used to seal the edges of the samples is the principal aberration evident in this first photograph. The second photograph (after 3 hrs. of exposure) shows evidence of rust on the untreated carbon steel sample as well as those samples treated at an energy of 200 eV and at

STAINLESS STEEL	→	$\frac{1.1}{1000}$	$\frac{2.8}{1000}$	$\frac{5.5}{1000}$	$\frac{11}{1000}$	$\frac{33}{1000}$
DOSE (mA min/cm ²)	→	$\frac{1.1}{500}$	$\frac{2.8}{500}$	$\frac{5.5}{500}$	$\frac{11}{500}$	$\frac{33}{500}$
ENERGY (eV)	→	$\frac{1.1}{500}$	$\frac{2.8}{500}$	$\frac{5.5}{500}$	$\frac{11}{500}$	$\frac{33}{500}$
UNTREATED CARBON STEEL	→	$\frac{1.1}{200}$		$\frac{5.5}{200}$	$\frac{11}{200}$	$\frac{33}{200}$

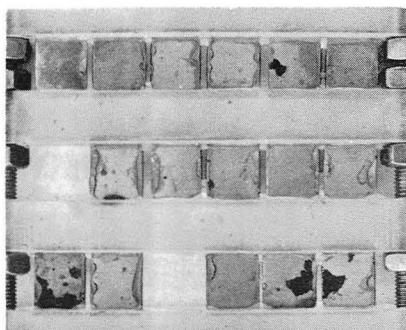
KEY
PRECORROSION IMPLANTATION CONDITIONS



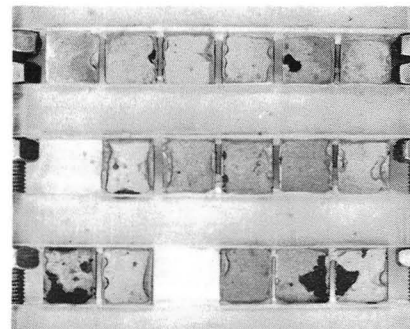
ZERO hr



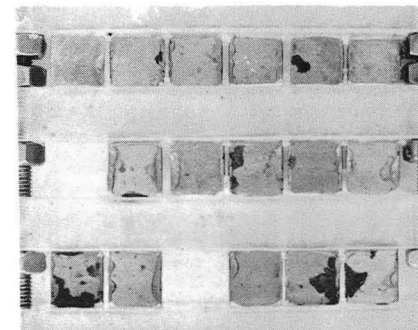
3 hrs



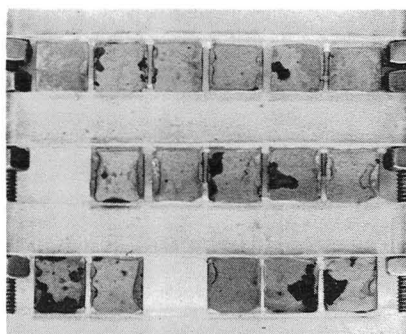
8 hrs



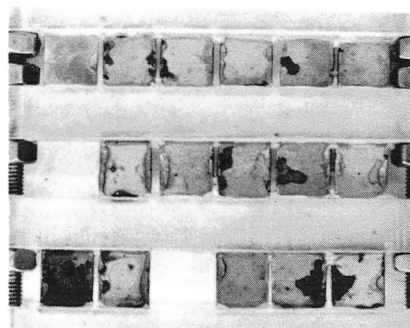
12 hrs



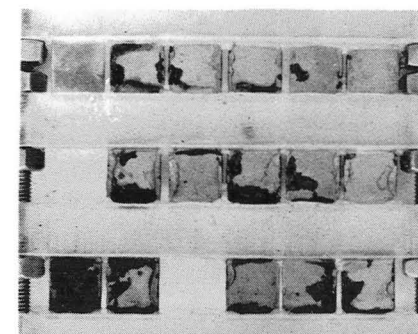
18 hrs



23 hrs



27 hrs



33 hrs

Fig. 3 Time History of Carbon Steel Corrosion in Warm, Moist Environment

low doses in the 500 eV samples. It is well to point out here that rust appears in the photographs as a dark spot. Lighter spots that can be seen on some samples appeared to be caused by residue from the condensed moisture rather than rust. While the first evidence of rust shown in the sequence of Fig. 3 is seen three hours after the test started, the first appearance of rust on the untreated sample was actually observed and photographed 15 min. after the start of the test. At this time, rust was not visible on any of the other samples. As time progressed during the test, additional rust spots began to appear on samples subjected to the greater doses and energies. The rust spot that appeared on the 11 mA min/cm² at 1000 eV sample after 8 hours of exposure is worthy of mention. It appeared that this as well as many other rust spots appearing on the treated samples actually originated at an edge where the moisture got under the epoxy and reached an untreated region. This was not the case with the untreated sample however because, as the three hour photograph shows, rust was initiated at various points over its entire surface. Many of the photographs seem to suggest that while a rust spot may get started at the edge of a treated sample its growth tends to be stopped after a short period of time. This is true for example of the 11/1000 sample which shows first evidence of a rust spot at 8 hours but no significant growth of this spot through the remaining 25 hours of the test. After 27 to 33 hours even the 33/1000 and 33/500 samples show small spots of rust (again originating near an edge). By comparing the appearance of the surfaces of these samples with that of the stainless steel one (upper left side of array) it is apparent that the treated carbon steel samples retain their aesthetically pleasing metallic appearance. At the 33 hour point it is also apparent that the untreated sample is by contrast completely rusted over.

Samples oxidized in the dry, oven environment showed the same general trends that were found in the moist, warm oxidation tests. That is, increases in mercury ion dose and energy tended to effect slower oxidation rates. This trend was apparent to the naked eye. Samples receiving the greater doses and energies appeared to exhibit more metallic, shiny surfaces compared to the untreated surfaces which tended to be a darker, brownish-red color. Optical reflectance measurements showed this same trend as a review of the raw reflectance data (Appendix B) will reveal.

Analysis of these data using the procedure outlined previously showed this same trend toward lower oxidation rates with dose and energy through the rate factor k_f . This factor was also found to be dependent on the temperature at which the oxidation was effected. Figure 4 shows for example the variation in rate factor with oxidation temperature for a typical surface treatment (2.8 mA min/cm^2 at 500 eV) assuming a first order reaction. Typically rate factor results like those of Fig. 4 which were based on the first order reaction seemed to fit the Arrhenius Equation (Eq. 4). Therefore all results represented here are based on the assumption that the reaction is first order. It is noteworthy however that when orders between zero and two were assumed in the data analysis the trends shown in Fig. 4 remained unaltered. It should be pointed out that analysis of the data in Fig. 4 were accomplished by using 0.024 as the reflectance of a rusted site at 6000 \AA (r_{FeO}°) and 0.546 as the reflectance of a metallic site at 6000 \AA (r_{Hg}°) in Eq. 2. These values were selected as typical of these two surface extremes based on reflectance measurements made on several highly oxidized and several unoxidized samples. Using values of these constants covering the measured ranges of variability (zero to 0.1 for r_{FeO}° and 0.5 to 0.6 for r_{Hg}°) in Eq. 2 yielded

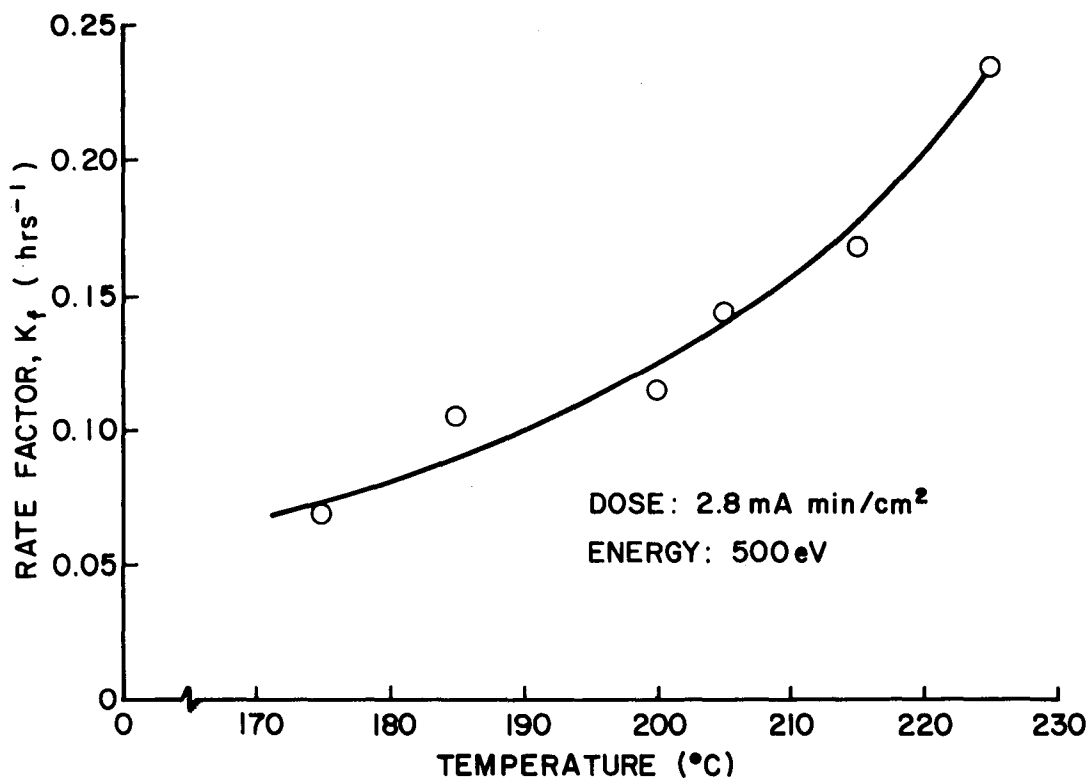


Fig. 4. Effect of Oxidation Temperature

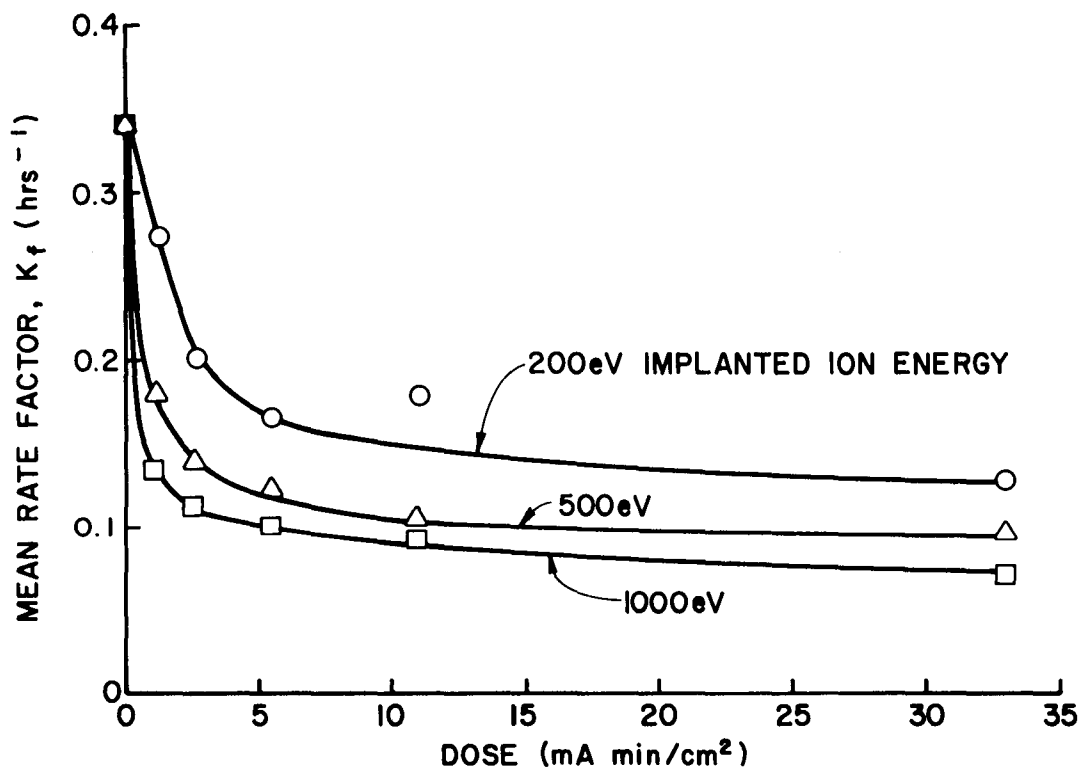


Fig. 5. Effects of Implanted Mercury Dose and Energy

about a 10% difference in numerical results, but the trends of Fig. 4 as well as those of the other figure to follow were again not altered by such changes.

The effects of implanted mercury dose and energy on the rate factors were generally apparent from the data taken at each oxidation temperature. As either dose or energy was increased, curves like the one in Fig. 4 were shifted to lower rate factor levels. In order to reduce the clutter associated with showing the effects of dose and energy however the mean value of the rate factor obtained from plots like those in Fig. 4 at a temperature of 200°C were selected and plotted as a function of dose and energy. The resulting plot is shown as Fig. 5. Considering the scatter generally associated with corrosion data the consistency of the results in Fig. 5 are considered to be very good. This figure shows the very dramatic effect of small mercury doses in retarding corrosion (reducing the rate factor). As higher doses are reached, further improvements in corrosion resistance are observed but the effect is seen to be less dramatic. Increases in ion energy are also observed to improve the corrosion resistance and the sensitivity to this parameter also seems to become less dramatic as implantation energy is increased. The results of Fig. 5 were based on the assumption of a first order reaction, but again the trends of this figure were not altered by this assumption.

An attempt was also made to fit the rate factor data to an Arrhenius expression (Eq. 4) in order to determine the variations in frequency factor and the activation energy associated the oxidation process as a function of the implantation conditions. Although relatively good fits to the experimental data like that of Fig. 4 could be obtained using Eq. 4 (~ 0.9 mean coefficient of determination), there seemed to be no

consistent trend in activation energies and frequency factors with implanted ion dose and energy. It is considered probable that trends were not apparent because of scatter in the reflectance data and the lack of a large enough statistical base to minimize the mean scatter. The mean activation energy taken from data for all implanted samples was 0.4 eV at a standard deviation of 0.08 eV.

Additional Results

To gain some understanding of the mechanism by which mercury might be enhancing the corrosion resistance of carbon steel, surface analysis of two oxidized samples (one implanted and one not implanted) were undertaken. Electron Chemical Surface Analysis (ESCA) was selected as the most promising tool for making the investigation. It was found that it is difficult to measure the mercury concentration in a sample because the dominant mercury signal occurs at a frequency close to a strong iron signal. The oxygen profile with depth was measured in these samples, and no significant difference in the oxygen depth profiles for the samples obtained with and without mercury implantation was apparent from the measurements made.

CONCLUSION

The corrosion resistance of carbon steel can be enhanced through the process of low energy mercury implantation from broad beam ion sources. Ion doses of the order of 10 mA min/cm^2 at implantation energies in the range of a few hundred to one thousand electron volts are sufficient to produce significant enhancement. In a moist, warm environment the onset of rusting can probably be extended from $\sim 15 \text{ min.}$ for a untreated sample to $\sim 30 \text{ hrs.}$ for one implanted at a dose of 33 mA min/cm^2 with

1000 eV mercury ions. This represents an increase of more than two orders of magnitude in the comparative durability of treated versus untreated steel in a very hostile environment. In less hostile environments the increased useful lifetime of ion implanted steels could be phenomenal. Additional research is needed to demonstrate protective effects that might be introduced with other implanted species. The adverse effects of abrasion on the beneficial effects of implanted mercury also needs to be studied.

REFERENCES

1. Day, Brian P., private communication, Royal Aircraft Establishment, Farnborough, Hants, England, Jan. 1979.
2. Anon., "Ion Implantation as a New Surface Treatment Technology," U.S. Department of Commerce Report AD/A-070-379, 1979.
3. Dearnaley, G., "The Use of Ion Beams in Corrosion Science," appears in Applications of Ions Beams to Metals, (Picraux, EerNisse and Voak, eds.) pp. 64f, Plenum Press, 1974.
4. Hirvonen, J. K., Treatise on Materials Science and Technology, Chaps 1 and 6, Academic Press, 1980.
5. Laidler, K. J., Chemical Kinetics, Chaps 1 and 3, McGraw-Hill, 1965.

APPENDIX A

The Qualities of and Equipment for Ion Implantation

Ion implantation is a relatively new technology that holds considerable promise in the area of surface treatments of materials. In particular the corrosion resistance, surface hardnesses and fatigue lifetimes of structural materials have been improved by using this process. Some of the relative advantages of this technology over other conventional surface treatment processes are:^{2,4}

- Almost any ion species can be implanted into almost any solid material. Differences in physical properties which prevent normal alloying or plating operations are not generally limited with this process.
- Ion implantation is a low-temperature process. It can often be added to the end of a production line without affecting existing operations. It is in fact possible to hold the base material temperature at almost any value considered desirable from other considerations during implantation.
- The surface of finished products can be treated without introducing significant dimensional changes and without changing bulk properties.
- The ion dose and energy can be easily controlled electrically by signals applied to the ion source.
- Novel nonequilibrium structures and metallurgical phases with properties that cannot be duplicated in bulk material can be produced at the surface.

- Ion implantation creates no problems of disposal of waste products, as does electroplating.
- The potential for reduction in the consumption of scarce metallic elements such as chromium is great because very small doses can be applied and accurate control can be achieved in applying them.
- Combinations of ions can be implanted in essentially any proportion so various beneficial effects associated with several alloying species can be achieved.
- It is possible to sputter clean a surface using inert ions before implanting. Because these processes are conducted in vacuo, contamination during the process is minimized. Further, the absence of a discontinuous interface between the implanted surface layer and the bulk material leads to excellent adhesion of the implanted layer.

The major drawback of the implantation technology has been its relatively high cost. This high cost has been a direct consequence of the fact that high purity implanters developed for the semiconductor industry have been used for most experiments conducted to date. The present research shows that similar beneficial corrosion resistance effects can be produced by using the considerably less costly broad beam ion sources. This makes ion implantation appear much more attractive as a surface treatment technique than it has heretofore been. The following table provides a comparison of the characteristics of the multiaperture, broad beam ion source and the single aperture high purity ion implanter.

Typical Implantation Equipment Performance Comparison

	Broad Beam Ion Source	High Purity Implanter
Beam Area (typical)	700 cm ² *	10 cm ² +
Beam Impurity Level	~ 10 ppm	< 1 ppm
Ion Typical Current Density (at target)	~ 1 mA/cm ² at 100 eV to ~ 10 mA/cm ² at 1 keV	~ 0.5 mA/cm ² @ 10 keV to ~ 0.02 mA/cm ² @ 1 keV
Operating Time to reach 10 ¹⁸ ion dose on 200 cm ² target using available source	16 sec (at 1000 eV or greater)	6000 sec (at 10 keV or greater)
Capital Cost **	\$100 K to \$200 K	\$200 K to \$2.6 M

* Rectangular broad beam ion sources that can be ganged together are also available so the size limitation is really determined by the size of the available vacuum system.

+ The beam is actually produced by scanning a 1 mm X 1 cm cross section beamlet over the target area.

** Including vacuum system.

The cost of applying a protective coating using a broad beam ion source is dependent on the total dose that would have to be applied. Based on results presented herein it appears that 10 mA min/cm² might be sufficient to effect the desired protection. Using data from the preceeding table for the broad beam ion source one can estimate an exposure time of a minute. If one assumes small medical and dental tools were being made then a typical surface area of a few cm² might be expected. If these were exposed in a 200 cm² beam ion source having an operating cost of about \$50/hr, one can estimate an impregnation cost a few cents per device.

One would expect this cost to come down in the future as the cost of ion beam equipment decreases. By contract the cost of doing the same job in a high purity implanter would be about one hundred times this amount.

APPENDIX B
 REFLECTANCE MEASUREMENTS
 of
 MERCURY IMPLANTED CARBON STEEL
 OXIDIZED IN A HOT, DRY ENVIRONMENT

				IMPLANTED ION DOSE (mA min/cm ²)																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
--	--	--	--	---	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

DISTRIBUTION LIST

Copies

National Aeronautics and Space Administration
Washington, DC 20546

Attn: RS/Mr. Del Williams, III	1
RTS-6/ Mr. Wayne Hudson	1
RTS-6/ Mr. Jerome Mullin	1
MT/ Mr. Ivan Bekey	1
ET-6/ Mr. Ed Sullivan	1

National Aeronautics and Space Administration
Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44135

Attn: Research Support Procurement Section	
Mr. B. Bane, MS 501-11	5
Technology Utilization Office, MS 3-19	1
Mr. S. Felder, MS 7-3	1
Report Control Office, MS 5-5	1
Library, MS 60-3	2
Mr. N. Musial, MS 500-113	1
Dr. M. Goldstein, Chief Scientist, MS 5-3	1
Mr. D. Petrash, MS 501-5	1
Mr. T. Cochran, MS 501-8	1
Mr. R. Finke, MS 77-4	1
Mr. B. Banks, MS 501-7	1
Mr. D. Byers, MS 501-7	1
Mr. W. Kerslake, MS 501-7	30

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

Attn: Dr. Jerry Smith, Code 472	1
---------------------------------	---

National Aeronautics and Space Administration
Marshall Space Flight Center
Huntsville, AL 35812
Attn: Mr. John Brophy

1

NASA Scientific and Technical
Information Facility
PO Box 8757
Baltimore, MD 21240
Attn: Accessioning Dept.

1

Case Western Reserve University
10900 Euclid Avenue
Cleveland, OH 44106

Attn: Dr. J. A. Mann Jr. (Chem Eng'g-A.W. Smith Bldg.) 1
Dr. J. F. Wallace (Met. & Mt'l. Sci.-White Bldg.) 1
Dr. W. H. Ko (Eng'g Design-Bingham Bldg.) 1
Dr. D. F. Gibbons (Bio. Med. Eng'g.-Olin Bldg.) 1

Royal Aircraft Establishment
Space Department
Farnborough, Hants
ENGLAND

Attn: Dr. D. G. Fearn 1
Mr. B. P. Day 1

Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91102

Attn: Technical Library 1
Mr. Eugene Pawlik 1
Dr. Graeme Aston 1

Electro-Optical Systems, Inc.
300 North Halstead
Pasadena, California 91107

Attn: Dr. R. Worlock 1
Mr. E. James 1
Mr. W. Ramsey 1

TRW Inc.
TRW Systems
One Space Park
Redondo Beach, California 90278

Attn: Dr. M. Huberman 1
Mr. H. Ogawa 1
Mr. Sid Zafran 1

National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California 94035
Attn: Technical Library 1

National Aeronautics and Space Administration
Langley Research Center
Langley Field Station
Hampton, Virginia 23365
Attn: Technical Library 1

Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, California 90265

Attn: Mr. J. H. Molitor
Dr. R. L. Poeschel
Dr. Jay Hyman
Dr. J. R. Beattie
Dr. W. S. Williamson

1
1
1
1
1

Princeton University
Princeton, NJ 08540

Attn: Mr. W. F. Von Jaskowsky
Dean R. G. Jahn
Dr. K. E. Clark

1
1
1

Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974

Attn: Dr. Edward G. Spencer
Dr. Paul H. Schmidt

1
1

Sandia Laboratories

Mail Code 5743

Albuquerque, NM 87115

Attn: Mr. Ralph R. Peters

1

Ion Tech, Inc.

P. O. Box 1388

1807 E. Mulberry

Fort Collins, Colorado 80522

Attn: Dr. Gerald C. Isaacson

1

EG & G Idaho

P. O. Box 1625

Idaho Falls, Idaho 83401

Attn: Dr. G. R. Longhurst, TSA-104

1

Mr. Curtis Haynes

Tektronix Inc.

M.S. 50-431

P. O. Box 500

Beaverton, Oregon 97077

1

Mass. Inst. of Tech.

Lincoln Laboratory

P. O. Box 73

Lexington, Mass. 02173

Attn: Dr. H. I. Smith

1

Mr. Jack Weigand 17920 South Watoloo Rd. Cleveland, OH 44119	2
Kent State University Canton, Ohio 44720 Attn: Dr. Gelerinter Dr. N. Spielberg	1 1
TME Corp. 16 Flagstone Drive Hudson, NH 03051 Attn: Mr. H. W. Jesse	1
Technics Corp. 7950 Cliny Ct. Springfield, VA 22153 Attn: Mr. Joel Weiner	1
Service du Confinement des Plasma Centre d'Etudes Nucleaires - F.A.R. B. P. 6 92260 Fontenay-aux-Roses FRANCE Attn: Dr. J. F. Bona	1
International Business Machines Corporation Thomas J. Watson Research Center P. O. Box 218 Yorktown Heights, NY 10598 Attn: Dr. Jerome J. Cuomo Dr. James M. E. Harper	1 1
IBM East Fishkill D/42K, Bldg. 300-40F Hopewell Junction, NY 12533 Attn: Dr. Chalres M. McKenna	1
Ion Beam Equipment, Inc. P. O. Box 0 Norwood, NJ 07648 Attn: Dr. W. Laznovsky	1
Optic Electronics Corporation 11477 Pagemill Road Dallas, TX 75243 Attn: Bill Hermann, Jr.	1
Circuits Processing Apparatus, Inc. 725 Kifer Road Sunnyvale, CA 94086 Attn: Spencer R. Wilder	1

Physicon Corporation
221 Mt. Auburn Street
Cambridge, MA 02138
Attn: H. von Zweck

1

Texas Instruments, Inc.
P. O. Box 225012
Dallas, TX 35265
Attn: Mr. Larry Rehn, MS34

1

Commonwealth Scientific Corporation
500 Pendleton Street
Alexandria, VA 22314
Attn: George R. Thompson

1

Veeco Instruments Inc.
Terminal Drive
Plainview, NY 11803
Attn: Norman Williams

1

CVC Products
525 Lee Road
P. O. Box 1886
Rochester, NY 14603
Attn: Mr. Georg F. Garfield, Jr.

1

Lawrence Livermore Lab.
P. O. Box 808
Livermore, CA 94550
Attn: Dr. Paul Drake, Mail Code L-437

1

Department of Electrical and
Computer Engineering
New Mexico State University
Las Cruces, NM 88003
Attn: Dr. Robert McNeil

1

